JC10 Rec'd PCT/PTO 18 JUN 2001

FORM PTO-1390 (REV. 5-93)	U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER **10537/132**
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 09/868447

INTERNATIONAL APPLICATION NO. **PCT/DE99/04018**	INTERNATIONAL FILING DATE **(17.12.99)** **17 December 1999**	PRIORITY DATES CLAIMED **(18.12.98)** **18 December 1998**

TITLE OF INVENTION
PROCESS FOR PRODUCING A THERMAL BARRIER COATING

APPLICANT(S) FOR DO/EO/US
STOLLE, Ralf; COSACK, Thomas; SCHWEITZER, Klaus and PULVER, Michael

Applicants herewith submit to the United States Designated/Elected Office (DO/EO/US) the following items and other information

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) immediately rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). (Unexecuted)
10. ☒ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
    ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☒ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information: An English translation of the International Search Report; Marked-up version of the Substitute Specification; one (1) sheet of formal drawings; copy of Form PCT/IB/306 and first page of the published International Application WO 00/37711.

EXPRESS MAIL NO. : EL327551190US

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U.S. APPLICATION NO (If known, see 37 C.F.R.1.5) 09/868447	INTERNATIONAL APPLICATION NO PCT/DE99/04018	ATTORNEY'S DOCKET NUMBER 10537/132

17. ☒ The following fees are submitted:

Basic National Fee (37 CFR 1.492(a)(1)-(5)):
Search Report has been prepared by the EPO or JPO $860.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) ... $690.00

No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) $710.00

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO $1,000.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) $100.00

				CALCULATIONS	PTO USE ONLY
ENTER APPROPRIATE BASIC FEE AMOUNT =				$ 860.00	
Surcharge of $130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				$	
Claims	Number Filed	Number Extra	Rate		
Total Claims	9 - 20 =	0	X $18.00	$	
Independent Claims	1 - 3 =	0	X $80.00	$	
Multiple dependent claim(s) (if applicable)			+ $270.00		
TOTAL OF ABOVE CALCULATIONS =				$ 860.00	
Reduction by ½ for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				$	
SUBTOTAL =				$ 860.00	
Processing fee of $130.00 for furnishing the English translation later the ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$	
TOTAL NATIONAL FEE =				$ 860.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40.00 per property +				$	
TOTAL FEES ENCLOSED =				$ 860.00	
				Amount to be: refunded	$
				charged	$ 860.00

a. ☐ A check in the amount of $__________ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. 11-0600 in the amount of **$860.00** to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-0600. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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18 June 2001
DATE

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EXPRESS MAIL CERTIFICATE

"EXPRESS MAIL" MAILING LABEL NUMBER EL327551190US

DATE OF DEPOSIT 6/18/01

TYPE OF DOCUMENT National Phase Patent App.
Re: Stolle, et al

SERIAL NO. To be Assigned FILING DATE Herewith

I HEREBY CERTIFY THAT THIS PAPER OR FEE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE "EXPRESS MAIL POST OFFICE TO ADDRESSEE" SERVICE UNDER 37 CFR 1.10 ON THE DATE INDICATED ABOVE, BY BEING HANDED TO A POSTAL CLERK OR BY BEING PLACED IN THE EXPRESS MAIL BOX BEFORE THE POSTED DATE OF THE LAST PICK UP, AND IS ADDRESSED TO THE ASSISTANT COMMISSIONER FOR PATENTS, WASHINGTON, D.C. 20231.

Miriam Sorola

(PRINTED NAME OF PERSON MAILING PAPER OR FEE)

Miriam Sorola

(SIGNATURE OF PERSON MAILING PAPER OR FEE)

process for producing a thermal barrier coating

09/868447
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[10537/132]

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor(s)	:	Ralf STOLLE et al.
Serial No.	:	To Be Assigned
Filed	:	Herewith
For	:	PROCESS FOR PRODUCING A THERMAL BARRIER COATING
Examiner	:	To Be Assigned
Art Unit	:	To Be Assigned

Assistant Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT AND
37 C.F.R. § 1.125 SUBSTITUTE SPECIFICATION STATEMENT

S I R:

Kindly amend the above-captioned application before examination, as set forth below.

IN THE SPECIFICATION AND ABSTRACT:

In accordance with 37 C.F.R. § 1.121(b)(3), a Substitute Specification (including the Abstract, but without claims) accompanies this response. It is respectfully requested that the Substitute Specification (including Abstract) be entered to replace the Specification of record.

IN THE CLAIMS:

On the first page of the claims, first line, change "Patent Claims" to --WHAT IS CLAIMED IS:--.

Please cancel, without prejudice, claims 1 to 12 in the underlying PCT application. Please also cancel, without prejudice, claims 1 to 9 in the annex to the International Preliminary Examination Report.

Please add the following new claims:

--10. (New) A method for producing a thermal barrier coating for a component of an internal-combustion engine, the component being exposed to hot gases, the thermal barrier coating having a columnar structure, comprising the steps of:

providing acetylacetonates of zirconium and at least one stabilizing element selected from the group consisting of alkaline earth metals and rare earths as starting substances;

vaporizing the starting substances by heating to at most 250°C so as to form coating gases;

transporting the coating gases in an admission system that has been heated to at most 250°C to the component; and

depositing the thermal barrier coating having a layer thickness between 25 μm and 1000 μm by heating a surface of the component to be coating at a deposition temperature between 300°C and 1100°C at a process pressure of between 0.5 mbar and 50 mbar so that the coating gases are broken down.

11. (New) The method according to claim 10, wherein the surface of the component to be coated is heated in the depositing step at a deposition temperature of between 800°C and 1100°C.

12. (New) The method according to claim 10, wherein the stabilizing element includes one of yttrium, lanthanum, calcium, magnesium and cerium.

13. (New) The method according to claim 10, further comprising the step of mixing the coating gases with a carrier gas.

14. (New) The method according to claim 13, wherein the carrier gas includes one of oxygen and a mixture of oxygen and argon.

15. (New) The method according to claim 13, wherein the coating gases and the carrier gas are transported to the component to be coated in the admission system.

16. (New) The method according to claim 10, wherein the starting substances are provided in the providing step in powder form.

17. (New) The method according to claim 10, wherein zirconia partially stabilized with 7% to 9% by weight of yttria is deposited in the depositing step.

18. (New) The method according to claim 10, wherein the thermal barrier coating is deposited in the depositing step on the component in a layer thickness of between 75 μm and 250 μm.--.

REMARKS

This Preliminary Amendment cancels, without prejudice, claims 1 to 12 in the underlying PCT Application No. PCT/DE99/04018. This Preliminary Amendment further cancels, without prejudice, claims 1 to 9 in the annex to the International Preliminary Examination Report and adds new claims 10 to 18. The new claims, inter alia, conform the claims to U.S. Patent and Trademark Office rules and do not add any new matter to the application.

In accordance with 37 C.F.R. § 1.121(b)(3), the Substitute Specification (including the Abstract, but without the claims) contains no new matter. The amendments reflected in the Substitute Specification (including Abstract) are to conform the Specification and Abstract to U.S. Patent and Trademark Office rules or to correct informalities. As required by 37 C.F.R. §§ 1.121(b)(3)(iii) and 1.125(b)(2), a Marked Up Version of the Substitute Specification comparing the Specification of record and the Substitute Specification also accompanies this Preliminary Amendment. Approval and entry of the Substitute Specification (including Abstract) is respectfully requested.

The underlying PCT Application No. PCT/DE99/04018 includes an International Search Report, dated April 28, 2000, a copy of which is included. The Search Report includes a list of documents that were considered by the Examiner in the underlying PCT application.

The underlying PCT Application No. PCT/DE99/04018 also includes an International Preliminary Examination Report dated February 23, 2001, an English translation of the annexed pages thereto are enclosed herewith.

It is respectfully submitted that the subject matter of the present application is new, non-obvious and useful. Prompt consideration and allowance of the application are respectfully requested.

Respectfully submitted,

KENYON & KENYON

Dated: 6/18/01

By:

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PCT

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Internationales Büro

INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

(51) Internationale Patentklassifikation [7] : C23C 16/40

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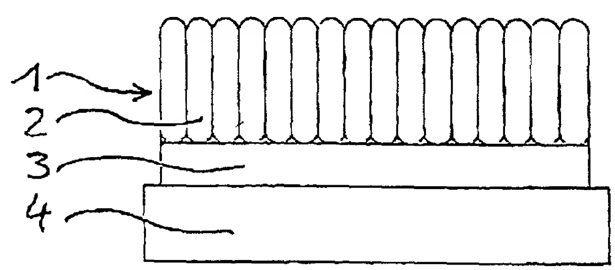
(81) Bestimmungsstaaten: US, europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Veröffentlicht
Mit internationalem Recherchenbericht.
Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist; Veröffentlichung wird wiederholt falls Änderungen eintreffen.

(54) Title: METHOD FOR PRODUCING A HEAT INSULATING LAYER

(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG EINER WÄRMEDÄMMSCHICHT



(57) Abstract

The invention relates to a method for producing a heat insulating layer. According to said method metallo-organic complexes of zirconium and at least one stabilizing element from the alkaline earth or rare-earth metals are used as starting material. The starting materials are evaporated by heating and the coating gases generated in this way are transported to a component (4) to be coated which is heated to a deposition temperature. The gases are then broken down such that a layer (1) is deposited on said component. To produce a heat insulating layer (1) with a columnar structure and of sufficient thickness the starting materials are heated at a process pressure of between 0.5 and 50 mbar to maximally 250 °C such that coating gases are produced and said coating gases are then transported to the component (4) to be coated whose surface is heated to a deposition temperature of between 300 °C and 1,100 °C.

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[10537/132]

11/PRTS

PROCESS FOR PRODUCING A THERMAL BARRIER COATING

The invention relates to a process for producing a thermal barrier coating, in which organometal complexes of zirconium and at least one stabilising element selected from the group of the alkaline earth metals or rare earths are provided as starting substances, the starting substances are evaporated by heating and the coating gases which are generated in this way are transported to a component to be coated, which is heated at a deposition temperature, where they are broken down so that a layer is deposited.

Electron beam physical vapour deposition (EB-PVD) processes, in which the substances which are to be deposited on the metallic component, such as for example zirconium oxide, are vaporized in a high-vacuum environment using an electron beam, are known for the production of thermal barrier coatings. On account of the considerable introduction of energy, a thin, molten zone is formed, from which the substances are vapourised and, in a condensation reaction, are deposited on the surface of the component. The layers produced in this way have a columnar structure which tolerates expansion, is better able to withstand alternating temperature stresses and leads to a prolonged service life.

Drawbacks of these processes are the extremely high installation costs for the electron beam gun, for the generation of the high vacuum, for the vacuum chamber and for the partial pressure control. Furthermore, those surfaces of the component which are not directly visible cannot be coated or can only be insufficiently coated during the coating cycle.

EP 0 055 459 A1 has disclosed a process for producing oxide layers by means of chemical vapour deposition (CVD), in which complexes derived from diketones, such as for example

acetylacetonate complexes, are mixed with steam in order to oxidise the metals contained in the complexes and are deposited on a substrate. In the process, the substrate is heated in various applications to temperatures of between 350°C and 800°C. The thicknesses of the deposited layers are in the range between 3.6 and 34 μm. The use of steam as a carrier gas has proven imperative, since oxygen does not enable either reproducibility or deposition to be achieved.

WO 94/21841 has disclosed a flame CVD process for applying inorganic layers to substrates, in which mixed oxides, such as yttrium-stabilised zirconia, are deposited at flame temperatures of from 300°C to 2800°C and pressures which lie well above ambient pressure. The starting substances for the coating gases are passed into the flame and, in a flame CVD process of this type, cannot be heated with a defined temperature cycle and transported to the substrate.

In known processes for producing thermal barrier coatings by means of chemical vapour deposition (CVD), it has hitherto only been possible to produce very thin layers with a low deposition rate and without a columnar structure, which layers also present poor adhesion and, moreover, contain relatively large quantities of undesirable carbon impurities. With a view to industrial use, the selection of the starting substances is of particular importance, since on the one hand they must not be too expensive and on the other hand they must be available in sufficient quantities.

The problem on which the present invention is based consists in providing a process for producing a thermal barrier coating of the generic type described in the introduction in which a thermal barrier coating with good layer properties and a columnar structure is produced as inexpensively as possible.

According to the invention, the solution to this problem is characterized in that the starting substances are heated, at a

process pressure of 0.5 to 50 mbar, to at most 250°C so that the coating gases are formed, and the coating gases are transported to the component to be coated, the surface of which is heated at a deposition temperature of between 300°C and 1100°C.

In this context, it has proven advantageous that thermal barrier coatings which contain zirconium oxide and, for example, yttrium oxide can be produced with a sufficiently great layer thickness of approximately 25 to 1000 μm using the process which is based on the chemical vapour deposition (CVD) principle. Moreover, the thermal barrier coatings produced in this way have a suitable crystal structure and morphology and required layer properties. In terms of their ability to withstand alternating temperature stresses, the layers are comparable to those produced using the EB-PVD process. A further advantage is that, unlike in the electron beam physical vapour deposition (EB-PVD) process, the scattering force of the process means that even those surfaces of the component to be coated which are not directly visible can be coated.

In a preferred configuration, organometal complexes, which are derived from diketones, of zirconium and at least one stabilising element selected from the group consisting of the alkaline earth metals or rare earths are provided as starting substances, since with these components the coating gases are completely broken down or burnt when they come into contact with that surface of the component which has been heated to deposition temperature. Moreover, they have the advantage over alkoxides that they are not sensitive to hydrolysis and are therefore easier to handle.

Furthermore, it is preferable for the coating gases to be mixed with a carrier gas, such as for example oxygen or a mixture of oxygen and argon.

In a further configuration of the process according to the invention, the coating gases or the coating gases and the carrier gas can be transported to the component to be coated, which is arranged in a receptacle, in an admission system which has been heated to at most 250°C.

It has proven expedient for the process to be carried out at a low process pressure of 0.5 to 50 mbar, in order that the coating gases or the coating gases and the carrier gas are transported as quickly as possible, so that their residence time in the hot zone produced by the thermal radiation of the component or substrate which has been heated to the deposition temperature is short as possible and to minimise vapour phase reactions.

Yttrium, lanthanum, calcium, magnesium or cerium are preferably provided as the stabilising element from the group consisting of the alkaline earth metals or rare earths, since they are not excessively expensive with regard to process costs and, furthermore, are available in sufficient quantities for industrial use.

Further configurations of the invention are described in the subclaims.

In the text which follows, the invention is explained in more detail on the basis of exemplary embodiments and with reference to a drawing, in which:

Fig. 1 shows a diagrammatic sectional view through a thermal barrier coating which has been produced using one exemplary embodiment of the process according to the invention, and

Fig. 2 shows a microscopic image of a thermal barrier coating which has been produced using an exemplary embodiment of the process according to the invention, in which image a columnar structure can be recognised.

Fig. 1 shows a thermal barrier coating, which is denoted overall by 1 and has a columnar structure 2, i.e. a fringe crystal structure, which has been deposited on a substrate 4 provided with an adhesion layer 3. In the present exemplary embodiment, the substrate 4 is a surface of a metallic rotor blade of a gas turbine around which hot gases flow in operation. Alternatively, the process can also be used, for example, to coat guide vanes of gas turbines or other parts of internal-combustion engines which are exposed to hot gases.

In the present exemplary embodiment of the process for producing a thermal barrier coating by means of chemical vapour deposition (CVD), first of all an adhesion layer 3 is applied to the surface of the rotor blade 4 around which hot gases flow using a conventional process. The adhesion layer 3 is preferably able to resist corrosion from hot gases and may, for example, be an aluminium diffusion layer, a platinum/aluminium diffusion layer or an MCrAlY cladding layer.

Then, the starting substances for the deposition of the thermal barrier coating 1 by means of chemical vapour deposition (CVD) are provided.

Acetylacetonate complexes of zirconium and yttrium which are in each case in powder form and are mixed in the appropriate ratio to form the desired layer stoichiometry are selected for these materials. Alternatively, the starting substances may also be vapourised separately and mixed in the vapour phase. The starting substances are vapourised or converted into the vapour phase by being heated to at most 250°C, so that the coating gases are formed, and are transported to the rotor blades 4 to be coated. They are transported by means of suitable carrier gases, such as for example oxygen or a mixture of oxygen and argon.

Moreover, those surfaces of the rotor blades 4 which are to be coated are heated, by means of a suitable heat source, at a deposition temperature of between 300°C and 1100°C. This ensures that the coating gases are not heated to over 250°C on their flow path to the rotor blades 4 to be coated. This is effected by, for example, using an admission system which has been heated to at most 250°C and is arranged so as to take account of the heat sources for the components or rotor blades 4, through which system the coating gases and the carrier gas are transported to that surface of the rotor blade 4 which is to be coated.

In the vicinity of those surfaces of the rotor blades 9 which have been heated to the deposition temperature, it may be impossible to completely prevent the coating gases from being heated to this extent on account of thermal radiation. In order to suppress the vapour phase reactions of the coating gases which are possible at elevated temperatures, the thermal barrier coating 1 is produced or deposited at relatively low process pressures of 0.5 to 50 mbar, so that they have a short residence time in the hot zones around the rotor blades 4 which have been heated to deposition temperature. To achieve the low process pressure required for the present vapour phase deposition, the process is carried out in a closed receptacle, to which a pump is connected.

When the coating gases come into contact with those surfaces of the rotor blades 4 which have been heated to deposition temperature, the chemical decomposition of the starting substances occurs and yttria-stabilised zirconia is deposited so as to form the thermal barrier coating 1 and gaseous by-products. Complete decomposition takes place on account of the high deposition temperatures. There are scarcely any carbon impurities. Furthermore, the thermal barrier coating 1 which has been deposited has a columnar structure 2 or fringe crystal structure which is able to tolerate expansion and is of benefit to the resistance to alternating temperature

stresses and to the service life of the thermal barrier coating 1. In the present process, the scatter which is achieved by exploitation of the aerodynamic flow conditions means that not only those surfaces of the rotor blades 4 which are directly visible or exposed to flow, but also all the other surfaces which are exposed to the flow of the coating gases and have been heated, are coated. The by-products are broken down in a downstream pyrolysis furnace and are then filtered and disposed off.

To improve the uniformity of coating, the rotor blades 4 may be moved inside the receptacle. Depending on how the process is controlled, it is possible to deposit thermal barrier coatings 1 with a layer thickness of approximately 25 to 1000 μm on the surfaces of the rotor blades 4, the layer thickness generally lying between 75 and 250 μm. Compared to rotor blades, the thermal barrier coatings 1 deposited on guide vanes of gas turbines often have higher layer thicknesses. To form the thermal barrier coatings 1, deposition in the present uses zirconia partially stabilized with 7-9% by weight of yttria. The process can be used for all parts of a gas turbine or other internal-combustion engines which are exposed to hot gases.

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Patent Claims

1. Process for producing a thermal barrier coating for components of internal-combustion engines which are exposed to hot gases, the thermal barrier coating having a columnar structure, characterized in that acetylacetonates of zirconium and at least one stabilising element selected from the group consisting of the alkaline earth metals or rare earths are provided as starting substances, the starting substances are vapourised by being heated to at most 250°C so as to form the coating gases, the coating gases are transported, in an admission system which has been heated to at most 250°C, to the component (4) to be coated, the surface of which is heated at a deposition temperature of between 300°C and 1100°C, where the gases are broken down, at a process pressure of from 0.5 to 50 mbar, so that a thermal barrier coating (1) with a layer thickness of between 25 μm and 1000 μm is deposited.

2. Process according to Claim 1, characterized in that the surface of the component (4) to be coated is heated at a deposition temperature of between 800°C and 1100°C.

3. Process according to Claim 1 or 2, characterized in that yttrium, lanthanum, calcium, magnesium or cerium is provided as the stabilising element selected from the group consisting of the alkaline earth metals or rare earths.

4. Process according to Claim 1 or 3, characterized in that the coating gases are mixed with a carrier gas.

5. Process according to one or more of the preceding claims, characterized in that oxygen or a mixture of oxygen and argon is provided as the carrier gas.

6. Process according to one or more of the preceding claims, characterized in that the coating gases or the coating gases

and the carrier gas are transported to the component (9) to be coated in the admission system,

7. Process according to one or more of the preceding claims, characterized in that the starting substances are provided in powder form.

8. Process according to one or more of the preceding claims, characterized in that zirconia partially stabilized with 7 to 9% by weight of yttria is deposited.

9. Process according to one or more of the preceding claims, characterized in that the thermal barrier coating (1) is deposited on the component (9) to be coated in a layer thickness of between 75 and 250 μm.

Abstract

A process for producing a thermal barrier coating, in which organometal complexes of zirconium and at least one stabilising element selected from the group of the alkaline earth metals or rare earths are provided as starting substances, the starting substances are evaporated by heating and the coating gases which are generated in this way are transported to a component (4) to be coated, which is heated at a deposition temperature, where they are broken down so that a layer (1) is deposited, in which process, in order to produce a thermal barrier coating (1) with a columnar structure and a sufficient layer thickness, the starting substances are heated, at a process pressure of 0.5 to 50 mbar, to at most 250°C so that the coating gases are formed, and the coating gases are transported to the component (4) to be coated, the surface of which is heated at a deposition temperature of between 300°C and 1100°C (Fig. 1).

09/868447

Fig. 1

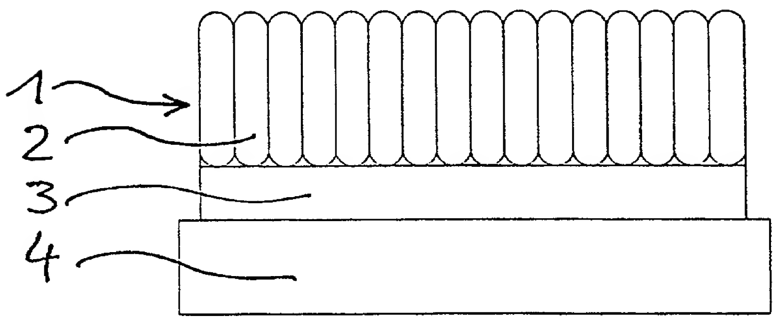
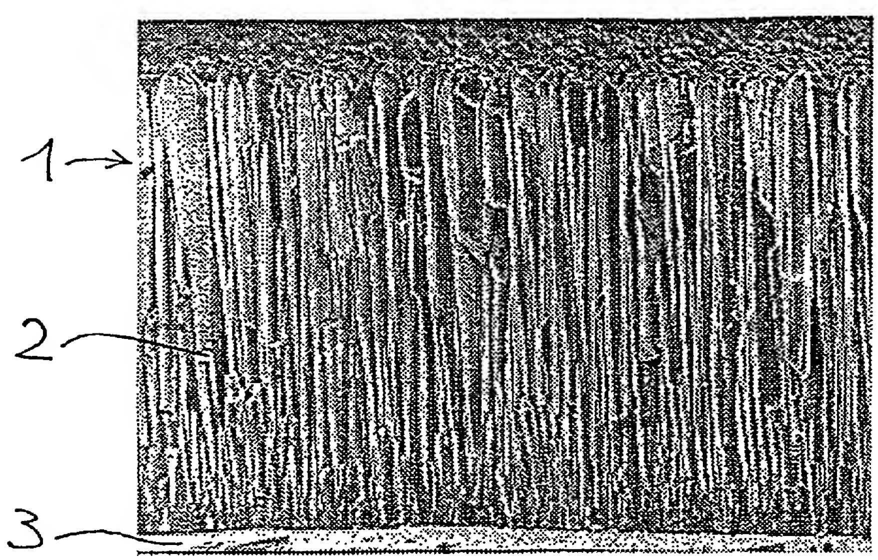


Fig. 2



PROCESS FOR PRODUCING A THERMAL BARRIER COATING

FIELD OF THE INVENTION

The present invention relates to a process for producing a thermal barrier coating, in which organometal complexes of zirconium and at least one stabilizing element selected from the group of the alkaline earth metals or rare earths are provided as starting substances, the starting substances are evaporated by heating and the coating gases which are generated are transported to a component to be coated, which is heated at a deposition temperature, where they are broken down so that a layer is deposited.

BACKGROUND INFORMATION

Electron beam physical vapor deposition (EB-PVD) processes, in which the substances that are to be deposited on the metallic component, such as, for example, zirconium oxide, are vaporized in a high-vacuum environment using an electron beam, are conventionally used for the production of thermal barrier coatings. On account of the considerable introduction of energy, a thin, molten zone is formed, from which the substances are vaporized and, in a condensation reaction, are deposited on the surface of the component. The layers produced in this manner have a columnar structure which tolerates expansion, is better able to withstand alternating temperature stresses and results in a prolonged service life.

Drawbacks of these processes are the extremely high installation costs for the electron beam gun, for the generation of the high vacuum, for the vacuum chamber and for the partial pressure control. Furthermore, those surfaces of the component that are not directly visible cannot be coated or can only be insufficiently coated during the coating cycle.

European Published Patent Application No. 0 055 459 describes a process for producing oxide layers by chemical vapor deposition (CVD), in which complexes derived from diketones, such as, for example, acetylacetonate complexes, are mixed with steam in order to oxidize the metals contained in the complexes and are deposited on a substrate. In the process, the substrate is heated in various applications to temperatures of between 350°C and 800°C. The thicknesses of the deposited layers are in the range between 3.6 and 34 μm. The use of steam as a carrier gas has proven imperative, since oxygen does not enable either reproducibility or deposition to be achieved.

International Published Patent Application No. WO 94/21841 describes a flame CVD process for applying inorganic layers to substrates, in which mixed oxides, such as yttrium-stabilized zirconia, are deposited at flame temperatures of between 300°C and 2800°C and pressures that are well above ambient pressure. The starting substances for the coating gases are passed into the flame and, in a flame CVD process of this type, cannot be heated with a defined temperature cycle and transported to the substrate.

In conventional processes for producing thermal barrier coatings by means of chemical vapor deposition (CVD), it has only been possible to produce very thin layers with a low deposition rate and without a columnar structure, which layers also present poor adhesion and, moreover, contain relatively large quantities of undesirable carbon impurities. Relative to industrial use, the selection of the starting substances is of particular importance, since they must not be too expensive and they must be available in sufficient quantities.

It is an object of the present invention to provide a process for producing a thermal barrier coating in which a thermal barrier coating with sufficient layer properties and a columnar structure is produced as inexpensively as possible.

SUMMARY

According to one example embodiment of the present invention, the starting substances are heated, at a process pressure of 0.5 to 50 mbar, to at most 250°C so that the coating gases are formed, and the coating gases are transported to the component to be coated, the surface of which is heated at a deposition temperature of between 300°C and 1100°C.

Thermal barrier coatings that contain zirconium oxide and, for example, yttrium oxide, may be produced with a sufficiently large layer thickness of approximately 25 to 1000 μm using the process that is based on the chemical vapor deposition (CVD) principle. Moreover, the thermal barrier coatings produced in this manner have a suitable crystal structure and morphology and required layer properties. In terms of their ability to withstand alternating temperature stresses, the layers are comparable to those produced using the EB-PVD process. A further advantage is that, unlike in the electron beam physical vapor deposition (EB-PVD) process, the scattering force of the process means that even those surfaces of the component to be coated that are not directly visible may be coated.

Organometal complexes, which are derived from diketones, of zirconium and at least one stabilizing element selected from the group consisting of the alkaline earth metals or rare earths are provided as starting substances, since with these components the coating gases are completely broken down or burnt when they come into contact with that surface of the component that has been heated to deposition temperature. Moreover, they have the advantage over alkoxides that they are not sensitive to hydrolysis and are therefore easier to handle.

Furthermore, the coating gases may be mixed with a carrier gas, such as, for example, oxygen or a mixture of oxygen and argon.

In a further example embodiment of the process according to the present invention, the coating gases or the coating gases and the carrier gas may be transported to the component to be coated, which is arranged in a receptacle, in an admission system that has been heated to at most 250°C.

The process may be performed at a low process pressure of 0.5 to 50 mbar, in order that the coating gases or the coating gases and the carrier gas are transported as quickly as possible, so that their residence time in the hot zone produced by the thermal radiation of the component or substrate that has been heated to the deposition temperature is as short as possible and to minimize vapor phase reactions.

Yttrium, lanthanum, calcium, magnesium or cerium may be provided as the stabilizing element from the group consisting of the alkaline earth metals or rare earths, since they are not excessively expensive with regard to process costs and, furthermore, are available in sufficient quantities for industrial use.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic cross-sectional view through a thermal barrier coating that has been produced using one example embodiment of the process according to the present invention.

Fig. 2 is a microscopic image of a thermal barrier coating that has been produced using an example embodiment of the process according to the present invention, in which image a columnar structure may be recognized.

DETAILED DESCRIPTION

Fig. 1 illustrates a thermal barrier coating 1, which has a columnar structure 2, i.e., a fringe crystal structure, which has been deposited on a substrate 4 provided with an adhesion layer 3. In the present example embodiment, the substrate 4 is a surface of a metallic rotor blade of a gas turbine around

which hot gases flow in operation. Alternatively, the process may also be used, for example, to coat guide vanes of gas turbines or other parts of internal-combustion engines which are exposed to hot gases.

In the present example embodiment of the process for producing a thermal barrier coating by chemical vapor deposition (CVD), an adhesion layer 3 is applied to the surface of the rotor blade 4 around which hot gases flow using a conventional process. The adhesion layer 3 may be able to resist corrosion from hot gases and may, for example, be an aluminum diffusion layer, a platinum/aluminum diffusion layer or an MCrAlY cladding layer.

Then, the starting substances for the deposition of the thermal barrier coating 1 by chemical vapor deposition (CVD) are provided.

Acetylacetonate complexes of zirconium and yttrium that are in powder form and are mixed in the appropriate ratio to form the desired layer stoichiometry are selected for these materials. Alternatively, the starting substances may also be vaporized separately and mixed in the vapor phase. The starting substances are vaporized or converted into the vapor phase by being heated to at most 250°C, so that the coating gases are formed, and are transported to the rotor blades 4 to be coated. They are transported by suitable carrier gases, such as, for example, oxygen or a mixture of oxygen and argon.

Moreover, those surfaces of the rotor blades 4 that are to be coated are heated, by a suitable heat source, at a deposition temperature of between 300°C and 1100°C. This ensures that the coating gases are not heated to over 250°C on their flow path to the rotor blades 4 to be coated. This is effected by, for example, using an admission system that has been heated to at most 250°C and is arranged so as to take account of the heat sources for the components or rotor blades 4, through

which system the coating gases and the carrier gas are transported to that surface of the rotor blade 4 that is to be coated.

In the vicinity of those surfaces of the rotor blades 9 that have been heated to the deposition temperature, it may be impossible to completely prevent the coating gases from being heated to this extent due to thermal radiation. In order to suppress the vapor phase reactions of the coating gases that are possible at elevated temperatures, the thermal barrier coating 1 is produced or deposited at relatively low process pressures of 0.5 to 50 mbar, so that they have a short residence time in the hot zones around the rotor blades 4 that have been heated to deposition temperature. To achieve the low process pressure required for the present vapor phase deposition, the process is performed in a closed receptacle, to which a pump is connected.

When the coating gases come into contact with those surfaces of the rotor blades 4 that have been heated to deposition temperature, the chemical decomposition of the starting substances occurs and yttria-stabilized zirconia is deposited so as to form the thermal barrier coating 1 and gaseous by-products. Complete decomposition occurs due to the high deposition temperatures. There are substantially no carbon impurities. Furthermore, the thermal barrier coating 1 that has been deposited has a columnar structure 2 or fringe crystal structure that is able to tolerate expansion and is of benefit to the resistance to alternating temperature stresses and to the service life of the thermal barrier coating 1. In the process according to the present invention, the scatter that is achieved by use of the aerodynamic flow conditions results in not only those surfaces of the rotor blades 4 that are directly visible or exposed to flow, but also all of the other surfaces that are exposed to the flow of the coating gases and have been heated, are coated. The by-products are

broken down in a downstream pyrolysis furnace and are then filtered and disposed of.

To improve the uniformity of coating, the rotor blades 4 may be moved inside the receptacle. Depending on how the process is controlled, it is possible to deposit thermal barrier coatings 1 with a layer thickness of approximately 25 to 1000 μm on the surfaces of the rotor blades 4, the layer thickness generally being between 75 and 250 μm. Compared to rotor blades, the thermal barrier coatings 1 deposited on guide vanes of gas turbines often have higher layer thicknesses. To form the thermal barrier coatings 1, deposition in the present uses zirconia partially stabilized with 7-9% by weight of yttria. The process may be used for all parts of a gas turbine or other internal-combustion engines that are exposed to hot gases.

[10537/132]

DECLARATION AND POWER OF ATTORNEY

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am an original, first and joint inventor of the subject matter that is claimed and for which a patent is sought on the invention entitled **PROCESS FOR PRODUCING A THERMAL BARRIER COATING,** the specification of which was filed as International Application No. PCT/DE99/04018, on December 17, 1999, an English translation of which is enclosed herewith.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims.

I acknowledge the duty to disclose information that is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate filed by me on the same subject matter having a filing date before that of the application on which priority is claimed:

PRIOR FOREIGN APPLICATION(S)

(Number)	(Country)	(Day/month/year filed)	Priority Claimed Under 35 USC 119	
198 58 701.5	Fed. Rep. of Germany	18 December 1998	Yes X	No _

And I hereby appoint Richard L. Mayer (Registration No. 22,490) my attorney with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

EL 243103 8020S

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PATENT TRADEMARK OFFICE

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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